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POLYMERIC THICKENERS FOR OIL-CONTAINING COMPOSITIONS

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664,483-4,886,660

BACKGROUND OF THE INVENTION

Field of the Invention

Polymer

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This invention relates to polymeric thickeners for oil-containing

Introduction to the Invention

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~~It is known to use polymers to thicken oil-containing compositions.~~
~~Reference may be made for example to U.S. Patent No. 5,318,995 (Mondet et al) and~~
~~U.S. Patent No. 5,736,125 (Morawsky et al), the disclosure of each of which is~~
~~incorporated herein by reference for all purposes.~~

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In U.S. Patent No. 5,736,125, the thickener is a copolymer containing (a) units containing a hydrophobic moiety, in particular an alkyl group containing 10 to 22 carbon atoms, a fluorinated alkyl group containing at least 6 carbon atoms, styrene, or an alkyl-substituted styrene in which the alkyl group contains 1 to 24 carbon atoms, and (b) units containing a hydrophilic moiety which is a carboxylic group, a dicarboxylic group, or a monoester or a monoamide of a dicarboxylic group, the units being derived from an alpha-beta ethylenically unsaturated carboxylic mono- or di-acid. No reference is made to the presence of other units. The copolymer has an acidity from about 0.1 to about 4.0 meq/g. The copolymers are for example copolymers of a long chain alkyl acrylate, and acrylic or methacrylic acid.

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In U.S. Patent No. 5,318, 995, the thickener is a copolymer which is defined as containing (a) 90 to 99% of units which have a first specified formula and which contain, in a side chain, a linear or branched hydrocarbon chain containing 4 to 22 carbon atoms, and (b) units which make up the remainder of the copolymer and which have a second specified formula containing, in a side chain, a carboxylic or sulfonic acid group which is at least partially present in the form of a salt. The copolymers are for example copolymers which consist of units derived from (a) an alkyl acrylate, methacrylate, acrylamide or methacrylamide, and (b) an acrylamido compound containing a carboxylic or sulfonic acid group, the copolymer having been treated with a suitable salt-forming compound to salify the carboxylic or sulfonic acid groups. The presence of other units is excluded by the definition.

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Further disclosure of the thickened oil-containing compositions is to be found in U.S. Patent Nos. 4,720,303, 4,737,541, 4,794,139, 4,839,166, 4,939,179, 4,971,722, 5,053,257, 5,086,142, 5,112,601, 5,192,462, 5,247,121, 5,256,737, 5,2700,379, 5,319, 5,255, 5,415,790, 5,422,233, 5,442,054, 5,516,544, 5,530,045, and 5,6100,202. The entire disclosure of each of those United States patents is incorporated herein by reference for all purposes.

SUMMARY OF THE INVENTION

I have discovered, in accordance with the present invention, that oil-containing compositions can be thickened with polymers which contain long chain alkyl groups in side chains but which contain no, or relatively few, acid groups as specified in U.S. Patent No. 5,736,125 or acid salt groups as specified in U.S. Patent No. 5,318,995. Furthermore, I have been able to obtain improved results through the use of such polymers. The polymers which are useful in the present invention are crystalline polymers, preferably side chain crystalline (SCC) polymers, which have a crystalline melting point, T_p , and an onset of melting temperature, T_o , such that $T_p - T_o$ is less than $T_p^{0.7}$; and which are soluble in the oil at temperatures above T_p . They must be dispersed in the oil by a process which comprises (i) dissolving the polymer in the oil at a temperature above T_p , and (ii) cooling the solution to crystallize the polymer in the oil. The polymer generally has at least one of (i.e. may have two or more of) the following characteristics which distinguish it from the SCC polymers previously disclosed as thickeners for oil containing compositions:

(i) it is a side chain crystalline (SCC) polymer which contains repeating units containing at least one group selected from oxygen-containing groups, e.g. a hydroxyl group; nitrogen-containing groups, e.g. N-alkyl amine, tertiary amine and pyrrolidinone groups; fluorine-containing groups; and silicon-containing groups, e.g. silyl groups;

(ii) it is a side chain crystalline (SCC) polymer which is substantially free of carboxylic groups, carboxylic groups in the form of salts, and sulfonic acid groups in the form of salts:

- (iii) it is a side chain crystalline (SCC) polymer which contains carboxylic acid groups in an amount less than 0.075 meq/g;
- (iv) it is a side chain crystalline (SCC) polymer which contains repeating units containing long chain alkyl groups containing at least 26 carbon atoms;
- (v) it is a side chain crystalline (SCC) polymer which is substantially free of functional groups;
- (vi) it is a side chain crystalline (SCC) polymer which is substantially free of ionized and ionizable groups;
- (vii) it is a side chain crystalline (SCC) polymer which is a block copolymer or a graft copolymer;
- (viii) it is a side chain crystalline (SCC) polymer which is a homopolymer;
- (ix) it is a main chain crystalline polymer; and
- ~~(x) it is a homopolymer or copolymer of caprolactone.~~

The composition must be maintained at a temperature below T_p , since the polymer will cease to have a thickening effect if it redissolves in the oil. The composition can be free of water, or can be a water-in-oil emulsion.

One of the advantages which results from the use of such polymers as thickening agents is that they reduce or remove the need to use surface active agents in water-in-oil emulsions. This is particularly useful in personal care products, since it is conventional for such products to contain surfactants which can cause an adverse reaction when they contact human skin. ~~I believe that this advantage will be observed with the known thickeners described in U.S. Patent No. 5,736,125, but not with those described in U.S. Patent No. 5,318,995. U.S. Patent No. 5,736,125 does not discuss the conventional use of surfactants, but it does contain a single specific Example, Example 3, in which no surfactant is used. In that Example, the oil is a silicone oil, and the SCC polymer contains units derived from methacrylic acid. The present invention also provides, therefore, a water-in-oil emulsion which is different from that disclosed in example 3 of U.S. Patent No. 5,736,125 and which comprises~~

- (1) an oil,

(2) dispersed in the oil, a polymer, preferably a side chain crystalline (SCC) polymer, which

- (a) has a crystalline melting point, T_p , and an onset of melting temperature, T_o , such that $T_p - T_o$ is less than $T_p^{0.7}$;
- (b) is soluble in the oil at temperatures above T_p , and
- (c) has been dispersed in the oil by a process which comprises
 - (i) dissolving the SCC polymer in the oil at a temperature above T_p , and
 - (ii) cooling the solution from step (i) to crystallize the SCC polymer in the oil; and
- (3) emulsified in the oil, water;

the composition being at a temperature below T_p ; and being substantially free from surfactants. Preferred compositions differ from the composition disclosed in Example 3 of U.S. Patent No. 5,736,125, in that they have one or both of the following characteristics

- (a) the oil is not a silicone oil;
- ~~(b) the SCC polymer is free from units derived from methacrylic acid.~~

DETAILED DESCRIPTION OF THE INVENTION

Definitions and Abbreviations

In this specification, parts and percentages are by weight. Temperatures are in °C. The onset of melting, T_o , the peak melting temperature, T_p , and the heat of fusion, J/g, are determined using a ~~DSC calorimeter~~ ^{differential scanning calorimeter (DSC), at} (at a rate of temperature change of 10°C/min, typically from -10 to 150 °C., and on the second heat cycle). The abbreviations Mn and Mw are used to denote number average and weight average molecular weight in daltons, respectively, measured in tetrahydrofuran using size exclusion chromatography, configured with a Wyatt laser light scattering detector. Bulk viscosities given in the ~~Examples~~ ^{Example} for the polymeric thickeners are in centipoise and were measured using a Brookfield LVT viscometer with an electrically thermostatted Thermosel heater, controlled for example to 95 °C., and small sample adapter using spindles 4 and 7. The procedure used in the ~~Examples~~ ^{Example} to compare the effectiveness of

the polymeric thickeners was as follows. 5 parts of the thickener ^{were} dissolved in 95 parts of hydrogenated polyisobutylene (HPIB) with stirring at 120 °C (HPIB is a light oil). The resulting solution was placed in an incubator at 20 °C. for 16 hours. The viscosity of cooled product in centipoise was determined using a Brookfield DV-I+ digital viscometer with CP-51 spindle using a sample adapter which was thermostatically controlled, for example, to 25 °C. The viscosities were measured after four minutes at a speed of 2.5 rpm, i.e. after 10 revolutions. The abbreviation CxA is used to denote an n-alkyl acrylate in which the n-alkyl group contains x carbon atoms, the abbreviation Cx alkyl is used to denote an n-alkyl group which contains x carbon atoms, and the abbreviation CxM is used to denote an n-alkyl methacrylate in which the n-alkyl group contains x carbon atoms. Other abbreviations are given elsewhere in the specification.

The Polymeric Thickeners

^{SCC} The polymers used as thickeners in the present invention are crystalline, this term being used to include polymers containing a crystalline polymeric moiety which is chemically bound to a non-crystalline moiety. The thickener can be a single polymer or a mixture of polymers, and the polymer can be a homopolymer, or a copolymer of two or more comonomers, including random copolymers, graft copolymers, block copolymers and thermoplastic elastomers. ~~Preferably at least part of the polymer is a side chain crystallizable (SCC) polymer.~~ The SCC polymer may for example be derived from one or more acrylic, methacrylic, olefinic, epoxy, vinyl, ester-containing, amide-containing or ether-containing monomers. The molecular weight of an SCC polymer is relatively unimportant to its T_p , but is generally an important factor in determining the T_p of other polymers. ~~The preferred SCC polymers are described in detail below.~~ However, the invention includes the use of other crystalline polymers having the desired properties. Such other polymers include, for example polymers in which the crystallinity results exclusively or predominantly from the polymer backbone, e.g. polymers of α -olefins containing 2 to 12, preferably 2 to 8, carbon atoms, e.g. polymers of monomers having the formula $CH_2 = CHR$, where R is hydrogen, methyl, propyl, butyl, pentyl, 4-methylpentyl, hexyl or heptyl, as well as other polymers such as polyesters, polyamides,

~~for example homopolymers and copolymers of caprolactone, and polyalkylene oxides,~~
~~for example polytetrahydrofuran.~~

It is important that the ^{SCC} polymer should melt over a relatively small temperature
 5 range. The closer T_p is to room temperature, the more rapid the transition should
 preferably be. Thus $T_p - T_o$ is less than $T_p^{0.7}$, particularly less than $T_p^{0.6}$, T_o and T_p being
 in ~~the~~ T_p can vary widely, depending on the conditions under which the composition is
 to be used, as further discussed below. $T_p - T_o$ is preferably less than 10°C , particularly
 less than 6°C .

The SCC polymers used in the present invention are in themselves well known.
 Publications describing SCC polymers include U.S. Patent Nos. 4,830,855, 5,120,349,
 5,156,911, 5,387,450, 5,412,035, 5,665,822, 5,783,302, ^{5,152,925, 5,807,291} ~~5,520,264, 5,607,291~~, 5,469,867,
 and 5,826,584; J. Poly. Sci. 60, 19 (1962), J. Poly. Sci. (Polymer Chemistry) 7, 3053
 15 (1969), 9, 1835, 3349, 3351, 3367, 10, 1657, 3347, 18, 2197, 19, 1871, J. Poly. Sci.,
 Poly-Physics Ed 18 2197 (1980), J. Poly. Sci. Macromol. Rev. 8, 117 (1974),
 Macromolecules 12, 94 (1979), 13, 12, 15, 18, 2141, 19, 611, JACS 75, 3326 (1953),
76; 6280, Polymer J 17, 991 (1985); and Poly. Sci USSR 21, 241 (1979). The
 disclosure of each of those U.S. patents ~~and publications~~ is incorporated herein by
 20 reference for all purposes.

The SCC polymer ~~preferably~~ used in this invention can be a homopolymer, or a
 copolymer of two or more comonomers, including random copolymers, graft
 copolymers, block copolymers and thermoplastic elastomers. The number average
 25 molecular weight of the SCC polymer is generally from 10,000 to 1,500,000, preferably
 12,000 to 1,000,000. ^{AA}
^{AA}
^{AA}

Preferred SCC polymers comprise side chains comprising linear polymethylene
 moieties containing 10 to 50, especially 14 to 22, carbon atoms, or linear perfluorinated
 30 or substantially perfluorinated polymethylene moieties containing 6 to 50 carbon atoms.
 Polymers containing such side chains can be prepared by polymerizing one or more
 corresponding linear aliphatic acrylates or methacrylates, or equivalent monomers such
 as acrylamides or methacrylamides. A number of such monomers are available
 commercially, either as individual monomers or as mixtures of identified monomers, for

example C12A, C14A, C16A, C18A, C22A, a mixture of C18A, C20A and C22A, a mixture of C26A to C40A, fluorinated C8A (AE800 from American Hoechst) and a mixture of fluorinated C8A, C10A and C12A (AE12 from American Hoechst). ~~Generally~~

~~the polymers also contain units derived from one or more other comonomers containing~~
 5 desired functional groups, for example the monomers listed below and equivalent monomers such as acrylamides and methacrylamides. In the list below, the term (meth) acrylate means that the compound may be either an acrylate or a methacrylate.

10 (a) Nitrogen-containing monomers, for example N,N-dialkyl amino (in particular, dimethylamino) (meth)acrylates; ammonium salt containing the (meth) acrylates, for example 2-trimethylammonium methylmethacrylate chloride, methacrylamidopropyl trimethylammonium chloride, N,N-(diethyl or dimethyl)aminoethyl(meth)acrylate methosulfate; N-vinylpyrrolidinone; imides like the ring-closed reaction products of maleic or itaconic anhydride with primary amines; 2-methacryloxy-N-ethylmorpholine; n or t-butylacrylamide; (meth)acrylamide; dimethylaminopropyl methacrylamide; 2-t-butylaminoethyl methacrylate; (meth)acrylonitrile; t-butylaminoethyl (meth)acrylate; acryloylmorpholine; N-(2-hydroxyethyl)acetamide and 1-piperidinoethyl (meth)acrylate.

20 (b) Oxygen-containing monomers, for example hydroxyalkyl (in particular, hydroxyethyl, hydroxypropyl, and hydroxybutyl) (meth)acrylates; tetrahydrofurfuryl (meth)acrylate; glycidyl methacrylate; alkoxyalkyl (meth)acrylate, e.g. methoxyethyl (meth)acrylate; 1-acryloxy-2-hydroxy-3-phenoxypropane; methylol methacrylate; ethoxyethyl (meth)acrylate; 2-(2-ethoxyethoxy)ethylacrylate; acetoacetoxyethyl (meth)acrylate; phenoxyethyl (meth)acrylate and (meth)acrolein.

30 (c) Fluorine-containing monomers, for example trifluoroethyl (meth)acrylate, heptafluorodecyl (meth)acrylate, octafluoropentyl (meth)acrylate, eicosafuoroundecyl (meth)acrylate, hexadecafluorononyl (meth)acrylate, and tetrahydroperfluorodecyl (meth)acrylate.

(d) Silicon-containing, e.g. silyl, monomers, for example trimethylsiloxy ethyl(meth)acrylate, 3-acryloxypropyl trimethoxysilane, and 3-acryloxypropyl ~~tris(trimethylsiloxy)silane.~~

When the SCC polymer is a graft or block copolymer, it can be formed either by copolymerizing a vinyl type macromonomer with other monomers, or by making an SCC polymer, and then reacting the functionalized polymer with the second block material, for example a urethane or epoxy block, polyethyleneoxide or polypropyleneoxide or polytetramethyleneoxide and the like polyether blocks, polysiloxane or poly(alkyl or alkoxy)silane blocks.

The SCC polymer should contain sufficient long chain groups that it will dissolve in the oil at the temperature above T_p . When the SCC polymer is used to thicken and oil, or mixture of oils, which is free from water, it generally contains at least 50 %, preferably at least 60%, particularly at least 80%, of units derived from a long chain monomer, and can contain up to 100% of such units. ~~When the SCC polymer is used to thicken a water in oil emulsion, it will generally contain at least 5%, preferably at least 10%, of units derived from a monomer containing a functional group, and may contain higher amounts, provided that the SCC polymer will dissolve in the oil.~~

The molecular weight of the thickening polymer should be sufficiently high that the polymer, after it has been dissolved in the oil, will precipitate from the oil when the heated mixture is cooled, for example to a temperature at least 10-20 °C. below T_p , thus producing an opaque mixture. This is believed to result in the formation of a polymer network in which the polymer crystallites are connected to one another by semisoluble chains.

The T_p of the thickening polymer is preferably ~~10-40 °C., particularly 10-30 °C., especially about 20 °C., above~~ the temperature at which the composition is to be used.

It appears that the oil plasticizes the thickening polymer, so that its melting point in the composition is for example 5-10 °C. lower than T_p , and it is therefore important that T_p is sufficiently above the temperature of use to ensure that the thickening polymer does not melt during use. Thus for compositions to be used at 20-25 °C. the thickening polymer preferably has a T_p of above 40 °C., preferably 40-50 °C. If the T_p of the thickening polymer is too far above the temperature of use, this can result in excessive precipitation of the polymer and a reduction in the thickening effect. It is preferred, therefore, that T_p is not more than 30 °C., preferably not more than 20 °C., above the temperature of use. Depending on the expected temperature of use, T_p may be from 0-150 °C. generally 10-100 °C. for example 20-80 °C.

~~The amount of the polymeric thickener preferably used varies with the application. It is usually unnecessary to use more than 10% of the total composition, and smaller amounts such as 3 to 7%, for example about 5%, are often effective.~~

Oils

~~The new polymeric thickeners are effective with a broad range of oils. Suitable oils are disclosed, for example, at column three, line 37, to column 4, line 4, of U.S. Patent No. 5,736,125, and elsewhere in the documents incorporated by reference herein.~~

Compositions

The new polymeric thickeners are useful for thickening a wide variety of compositions. The compositions can be free from water, or can be water-in-oil emulsions. The invention is particularly useful for personal care compositions, for example cosmetics, toiletries, and cleansers, including but not limited to lipsticks, deodorant sticks, nail varnishes, creams and gels and oils including sun creams, protective hand creams, night renewal creams, body milks and lotions, light facial cream, protective day cream, liquid moisturizing emulsions, oil-in-water creams, water-in-oil creams, and the like and well as thickened oil products with or without water, as well as those designed to assist in removing other cosmetic, makeup or personal care products. However, the invention is also useful in other contexts, for example in paints,

film forming compositions, inks, and compositions carrying active ingredients such as UV absorbers, fragrances, biocides, antimicrobial agents, germicides, antioxidants, preservatives, disinfectants, enzymes, nutrients, minerals, and drugs (including pharmaceuticals which are active physiologically or pharmacologically, either topically or systemically) as well as other uses disclosed in the documents incorporated by reference. ~~Compositions containing a thickener containing an ammonium salt are likely to be useful in certain types of hair care compositions.~~

~~Example~~

Example.

The invention is illustrated by the following ~~Examples, some of which are comparative examples.~~ ~~Example~~

Example
Examples

~~Polymers and copolymers were made using the ingredients and amounts thereof shown in the Table below, using the following generalized method. To a resin kettle equipped with overhead stirrer and condenser was added 20% of the monomers and chain transfer agents. The mixture in the resin kettle was heated to 110 °C., and oxygen was removed from the system through nitrogen purge for about 30 min followed by addition of 20% of the starting initiator charge. After allowing sufficient time for any initial exotherm to abate, the remaining monomers, chain transfer agents and starting initiator were pumped into the reaction vessel over 60-90 min. The polymer mixture was allowed to continue reacting for 60 min followed by addition of the chase initiator and reaction for 60 min. The mixture was put under reduced pressure for 60 min to removal volatile residuals. The resulting polymers were generally yellow to white solids.~~

The molecular weight, T_p , and viscosity of each sample was measured. The effectiveness of the polymers as thickeners for HPIB was measured as described above, and the results are shown in the Table below. The following abbreviations are used in the Table. ME = mercaptoethanol; ~~VIA~~ = methacrylic acid; NVP = N-vinylpyrrolidinone; DMAEA = N,N-dimethylaminoethyl acrylate; HEA = 2-hydroxyethyl acrylate; TAPO = t-amylperoxy 2-ethylhexanoate sold by Witco as Esperox 570P, 75% active in liquid; TBPB = t-butylperoxybenzoate sold by Witco as Esperox 10; and opq = ~~opaque in appearance.~~

P.S.
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TABLE

| Example | 1 | 2* | 3 | 4* | 5 | 6 | 7 | 8 |
|----------------|------------|---------|----------|-----------|----------|----------|----------|----------|
| C16A | | | | 95 | | | | |
| C18A | 80 | | 95 | | 100 | 85 | 85 | 85 |
| C22A | | 95 | | | | | | |
| HEA | 20 | | | | | | | |
| NVP | | | | | | 15 | 15 | |
| DMAEA | | | | | | | | 15 |
| MA | | 5 | 5 | 5 | | | | |
| ME | 0.34 | 0.17 | 0.17 | 0.17 | 0.17 | 0.34 | 0.34 | 0.1 |
| TAPO | 1.73 | 1.73 | 1.73 | 1.73 | 1.73 | 1.73 | 1.73 | 1.73 |
| TAPB | 0.67 | 0.67 | | | | 0.67 | 0.67 | |
| TBPB | | | 0.5 | 0.5 | 0.5 | | | 0.5 |
| Tp °C. | 48 | 67 | 47 | 39 | 50 | 48 | 46 | 45 |
| J/g | 56 | 99 | 57 | 64 | 73 | 29 | 61 | 60 |
| Mw | 236K | | 427K | 1,000K | 950K | | | |
| Mn | 52K | | 240K | 520K | 230K | | | |
| Bulk viscosity | 4,000 | 2,500 | 19,000 | 24,000 | 2,000 | 3,950 | 4,000 | 350 |
| Visc in HPIB | 12,600 opq | 164 opq | 2600 opq | <50 clear | 5400 opq | 5100 opq | 6200 opq | 6000 opq |

* denotes comparative example.